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The Magneto-Electric Properties of RMnO_3 Compounds

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Abstract. The RMnO_3 compounds adopt the orthorhombic perovskite crystal structure for large rare earth ions R, and a hexagonal crystal structure for small rare earth ions. In both crystal structures, the rare earth ions occupy non-centered positions which can result in long-range dipolar order at low temperature. Consequently, these materials exhibit coexistence of magnetic and electric ordering. The crystal packing and chemical bonding of these open-shell systems provides information about mechanisms of magneto-ferroelectric ordering and magneto-electric coupling.

1 Introduction

Multiferroics are materials that simultaneously exhibit more than one type of ordering. The simultaneous occurrence of magnetic and electric order of magneto-ferroelectrics is particularly interesting as it combines properties that could be utilized for information storage, processing and transmission. It allows both magnetic and electric fields to interact with magnetic and electric order. However, this property is rare as the existence of partially filled atomic orbitals, prerequisite for magnetic dipoles or moments, usually precludes the occurrence of local electric dipoles, which are typically associated with the presence of either empty *d*-shells and/or an electron lone-pair configuration.

Ferromagnetic materials are commonly used for non-volatile information storage in tapes, hard drives, etc. They are also used for information processing due to the interaction of electric current and light with magnetic order. Ferroelectrics find applications due to their large piezoelectric coupling constant, i.e., the coupling between an electric field and strain. This effect is utilized in devices such as capacitors, microphones and transducers where a voltage can generate strain and vice versa. Ferroelectric materials not only exhibit piezoelectric coupling, common for most materials that lack inversion symmetry, but also possess memory functionality. The electric polarization remains finite after removing an applied electric field. This property can be exploited in non-volatile memory devices, where the information stored in the electric polarization is retained, even after removing the power of the device. Much interest is being generated by the magneto-ferroelectrics. The simultaneous magnetic and electric order makes it possible for the magnetic

polarization to be addressed or switched not only by applying a magnetic field but also by an electric field, or likewise that the electric polarization can be addressed or switched by applying an electric and/or a magnetic field. This property enables completely new device architectures to be designed. Furthermore, it is of interest to materials scientists to understand the associated chemical bonding. This will allow them to circumvent the prevalent mutual exclusion of magnetic and electric dipoles by smart materials engineering in bulk compounds or thin films.

In this manuscript, I focus on two mixed rare earth-transition metal oxides, the orthorhombic perovskites RMnO_3 , stable for large ionic radius R , and the hexagonal compounds RMnO_3 , stable for small ionic radius R . The crystal structure and local coordination numbers are completely different for the two structure types. In the perovskites, the R^{3+} is coordinated by 12 oxygen ions. In the hexagonal RMnO_3 structure, the R^{3+} is coordinated by seven oxygen ions, consisting of a trigonal antiprismatic coordination of six plus one additional ion.

2 ABO_3 Perovskites

This structure class encompasses many ferroelectric materials such as BaTiO_3 , and can be constructed from corner-sharing BO_6 octahedra, and the A-ion is coordinated by eight octahedra (see Fig. 1). A ferroelectric moment can in part be derived from a lone-pair ion on the A-site, such as Pb^{2+} or Bi^{3+} , and in part from a small transition metal ion, with d^0 electron configuration on the B-site. Both mechanisms can result in long-range dipolar order [1]. Magnetism can be generated by a magnetic rare earth ion on the A-site and/or by a magnetic transition metal ion on the B-site, such as Mn^{3+} or Fe^{3+} . However, because transition metal ions generate either magnetic (d^n state) or electric moments (d^0 state), magnetic and electric order on the same site is in conflict. A judicious choice of composition can lead to ferroelectromagnetism in compounds such as $\text{Pb}(\text{Fe}_{0.5}\text{W}_{0.5})_3$, and various other combinations. Therefore, the magnetic and electric moments may be dilute, which typically results in ordering at suppressed temperatures. Nevertheless, this approach can be successful, and the overview of *Smolenski* and *Chupis* lists a number of such ferroelectromagnets [2].

Within this class of perovskites, BiFeO_3 and BiMnO_3 have received considerable attention. They are difficult to prepare as stoichiometric materials and require special synthesis conditions. Both have been grown as thin films by pulsed laser deposition (PLD). BiFeO_3 is both ferroelectric and antiferromagnetic at room temperature, which triggers interest for devices. Recent reports of ferromagnetic coupling [3] provide evidence of strong dependence on the oxygen stoichiometry [4]. A non-stoichiometric composition may thus trigger desirable magnetic interactions, but it also increases the electrical conductivity, possibly preventing the application of sufficient electric

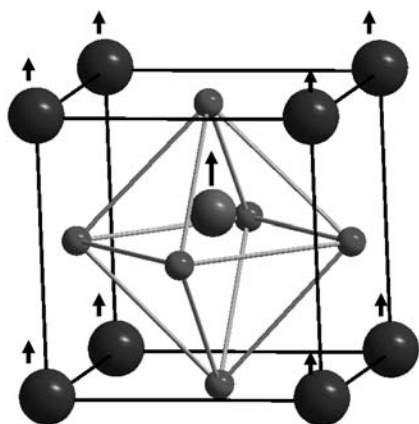


Fig. 1. Crystal structure of a perovskite ABO_3 . The transition metal B-ions are located near the center of the cube coordinated by an oxygen octahedron. The A-ions are located at the corner of the cube. The *arrows* indicate a tetragonal ferroelectric distortion

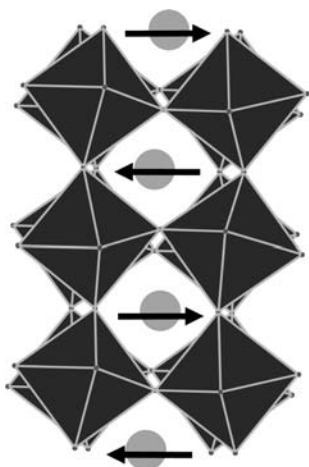


Fig. 2. Crystal structure of an orthorhombic perovskite RMnO_3 . The Mn-ions are located in the center of the coordinating oxygen octahedra. The R-ions are coordinated by eight octahedra or 12 O-ions, but displaced from the center in an anti-polar fashion, as indicated by *arrows*

fields by electrodes. Ferromagnetism in oxides is often mediated by double exchange interactions, which render a material metallic, screening electric dipoles. Ferromagnetism in ferroelectromagnets should therefore be the result of different interactions, such as single ion anisotropy or Dzyaloshinskii–Moriya coupling, resulting in a canted antiferromagnetic state. Furthermore, the progress in theoretical understanding of the chemical bonding associated with ferroelectricity has impacted greatly on the understanding of magneto-ferroelectrics [5].

The discovery of ferroelectricity resulting from competing magnetic interactions in the perovskites TbMnO_3 and DyMnO_3 [6, 7] has attracted much recent attention and has opened the field to a completely different approach to generating ferroelectricity in oxides. These materials were known as orthorhombic compounds with Pnma (the conventional setting of Pbnm) space

group symmetry. This space group exhibits inversion symmetry and thus no ferroelectric order was expected. However, the Mn^{3+} -spins in TbMnO_3 order in an incommensurate fashion near 40 K, which then gives rise to a ferroelectric moment at a lock-in transition, near 30 K, below which the incommensurate magnetic wave vector becomes temperature independent. Below this lock-in transition, the electric polarization becomes finite and can be reversed by an electric field. The origin of the emergence of the electric order is not fully understood, but seems to be associated with two competing magnetic orders. The large ionic radius elements on the A-site, such as LaMnO_3 , give rise to A-type antiferromagnetic order of the Mn-spins, whereas the small ionic radius A-site elements, from HoMnO_3 onwards, promote E-type antiferromagnetic order [8]. Small ionic radius A-site cations reduce the Mn–O–Mn bond angles from 180° for cubic materials to values less than 145° . At these bond angles, the perovskite structure is strongly distorted and not only the nearest neighbor magnetic interactions are relevant, but also the next-nearest neighbor interactions. Thus, the magnetic order changes from two antiferromagnetically (AF) and four ferromagnetically (FM) coupled neighbors for A-type order to four AF and two FM coupled neighbors for E-type order. At intermediate bond angles, incommensurate order is stabilized [9], the inversion symmetry is broken and this induces the electric polarization. A strong magneto-electric coupling is evidenced by large magneto-capacitance effects, where the dielectric constant changes by more than a factor 5 on applying a magnetic field of 4 T in DyMnO_3 [7]. Furthermore, lattice modulations that are coupled to the magnetic modulation have been detected. The nature of the ferroelectric transition is likely to be improper, where the ferroelectric state is driven by the magnetic ordering. The electric polarization is relatively small, with values lower than $0.2 \mu\text{C}/\text{cm}^2$.

3 AMnO_3 Hexagonal Manganites

Despite the compositional identity with the perovskites, these materials are structurally completely different. They consist of sheets of MnO_5 triangular bipyramids connected by AO_7 polyhedra. The magnetic ordering is derived from the electronic d^4 configuration of Mn^{3+} on the B-site, and from a magnetic rare earth ion on the A-site. Despite conclusions to the contrary in early structure determinations, the Mn^{3+} is located close to the barycenter of the bipyramid [10, 11], and the ferroelectric moment is largely derived from the A^{3+} -motion in its coordination sphere.

The structure is stable for small rare earth ions on the A-site, including yttrium, and for Mn^{3+} on the B-site. The Mn^{3+} -ion stabilizes the structure by a ligand field effect, because the crystal field splitting of the d^4 configuration in a triangular bipyramid results in a non-degenerate electronic state. For all

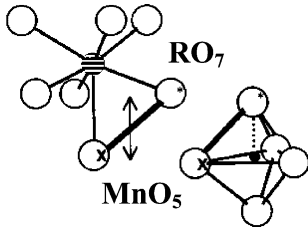


Fig. 3. Local coordination of rare earth R- and Mn-ions in hexagonal RMnO_3 . The R-ion is coordinated by $6 + 1$ O-ions and the Mn-ion is coordinated by 5 O-ions forming a trigonal bipyramid (taken from [10, 11])

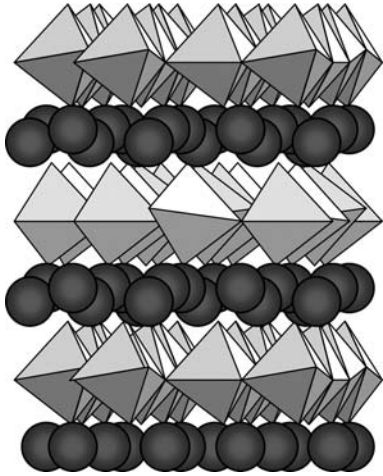


Fig. 4. Crystal structure of a hexagonal manganite RMnO_3 , with R a rare earth element, with ferroelectric distortion. The Mn-ions are located near the barycenter of the trigonal bipyramids of O-ions. The distortion of the Y-layer (*open circles*) is clearly observable (reproduced from [10, 11])

other transition metals on the B-site, and large ionic radius elements on the A-site, the perovskite structure is preferred [12, 13].

These materials were intensely studied in the 1960s, during which time the crystal and magnetic structures were investigated [14]. The ferroelectric ordering sets in above 1000 K, while antiferromagnetic ordering of the Mn-spins occurs near 75 K, with small variations for different R rare earth ions. These ordering temperatures indicate that RMnO_3 are proper ferroelectrics, which is in line with a polarization of $5 \mu\text{C}/\text{cm}^2$ and large displacements inside the unit cell due to the electric ordering. Various corresponding indates RInO_3 and gallates RGaO_3 are also reported or predicted to be ferroelectric (see review in [12]). The magneto-electric coupling is evidenced by anomalies in the temperature dependence of the dielectric constant at the magnetic ordering [15, 16]. The coupling was convincingly shown by *Fiebig* et al. in non-linear optical experiments, which mapped both electric and antiferromagnetic domain walls [17]. Furthermore, *Lottermoser* et al. showed that in HoMnO_3 , ferromagnetic ordering of the Ho-spins could reversibly be switched on and off by using an electric field, again indicating the magneto-electric coupling [18]. There have been conflicting results from studies of the nature of the ferroelectric ordering. After the discovery of the

ferroelectric properties of this class of materials by *Bertaut* et al. [14], several transition temperatures were reported. Measurements of the pyroelectric current by *Ismailzade* et al. of YMnO_3 showed the ferroelectric ordering to be near 930 K [19]. A transition at 1270 K was recorded for YMnO_3 , associated by *Lukaszewicz* et al. with a tripling of the lattice [20]. *Van Aken* et al. redetermined the crystal structures of several RMnO_3 and found, in contrast with earlier reports, that Mn^{3+} is close to the barycenter of the coordinating oxygen bipyramid [10, 11]. They concluded that the ferroelectric moment is mostly associated with the relative motion of the R-ion and its coordinating oxygens [21]. Subsequent neutron diffraction experiments up to 1400 K by *Lonkai* et al. did not reveal any significant coupling to the modes responsible for the ferroelectric transition [22]. They concluded that RMnO_3 must be an improper ferroelectric, in agreement with a theoretical analysis of the displacements [23]. *Nénert* et al. argue, based on synchrotron single crystal diffraction and a group theoretical analysis, that these materials are proper ferroelectrics [24], in agreement with the result of *Ismailzade* et al. [19]. The situation requires further measurements and analysis.

4 Novel Mechanisms

The concept of generating ferroelectricity from geometric magnetic frustration has resulted in theoretical and experimental efforts to formulate new mechanisms. *Van Aken* et al. proposed that the ferroelectric state in YMnO_3 is generated by geometric, rather than electronic effects [21]. *Efremov* et al. have proposed that frustration of electronic degrees of freedom other than magnetic interactions may result in ferroelectricity [25]. They predicted that charge ordering in orthorhombic manganites can result in a ferroelectric state. In charge-ordered manganites, the manganese ions can adopt two valence states, Mn^{3+} and Mn^{4+} , which order in a regular pattern below the charge ordering temperature. Various charge ordering symmetries have been observed for $(\text{La,Ca})\text{MnO}_3$. Such charge order can be site-centered, with a spherical charge distribution around the nucleus, or bond-centered, in which electron density is concentrated between two nuclei. For partial bond-centered and partial site-centered charge ordering, *Efremov* et al. calculated the emergence of a ferroelectric state [25]. It seems natural to expect that future studies of other systems with competing interactions such as orbital orderings will generate novel improper ferroelectrics. In addition, systems with cationic ordering can be expected to show ferroelectric states. Here, the non-centered coordination of RO_7 , RO_9 , or RO_{12} clusters can be exploited.

5 Conclusions

Ferroelectromagnetic systems, with coexistence of magnetic and electric moments, can be observed in a selected number of compounds. Conventionally, such coexistence is precluded because magnetic systems require unfilled d - or f -orbitals, whereas electric moments are generated by empty d -orbitals or an electron lone-pair configuration. The rare earth ion is special because the magnetism, generated by unfilled $4f$ -orbitals, is shielded by filled valence shells. This can lead to magneto-ferroelectric states in both orthorhombic perovskites ABO_3 and hexagonal AMnO_3 . In addition, novel mechanisms including charge ordering may lead to novel magneto-ferroelectric compounds.

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